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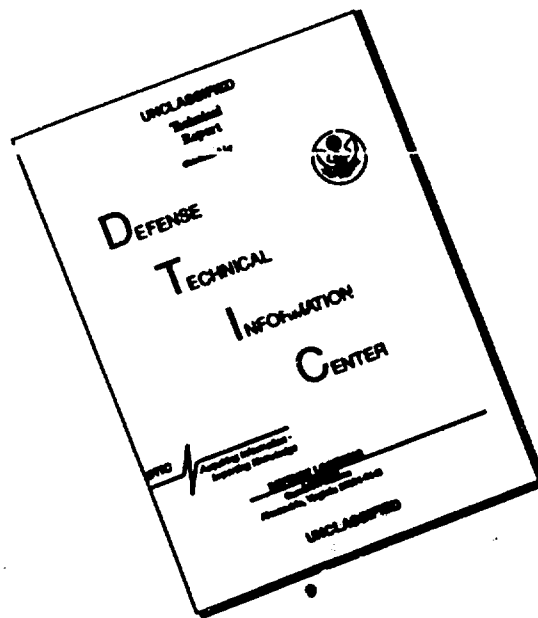
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Several metallization schemes using refractory metals have been demonstrated to produce ohmic contacts to diamond via a solid-state reaction process. This process utilizes existing microelectronic techniques and provides strongly adherent contacts which exhibit low contact resistance. Measurements of the long-term reliability of Mo/Au contacts formed by this process on a type IIb diamond crystal are presented here for the temperature range 450 to 625°C. The measurements consist of the resistance between two contacts as a function of isothermal annealing time over time intervals in excess of 130 h in a purified inert ambient. The Mo/Au contacts appeared to be stable and reliable at these high temperatures with no indications of deterioration or degradation of performance.

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High Temperature Reliability of Refractory Metal Ohmic Contacts to Diamond

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ABSTRACTS

Several metallization schemes using refractory metals have been demonstrated to produce ohmic contacts to diamond via a solid-state reaction process. This process utilizes existing microelectronic techniques and provides strongly adherent contacts which exhibit low contact resistance. Measurements of the long-term reliability of Mo/Au contacts formed by this process on a type IIb diamond crystal are presented here for the temperature range 450 to 625°C. The measurements consist of the resistance between two contacts as a function of isothermal annealing time over time intervals in excess of 130 h in a purified inert ambient. The Mo/Au contacts appeared to be stable and reliable at these high temperatures with no indication of deterioration or degradation of performance.

The need for electronic devices which will operate reliably in the temperature range from 400 to 600°C has made it essential to look beyond conventional electronic materials such as silicon or gallium arsenide. Devices based on these materials are presently able to meet a limited number of elevated temperature demands but only with the added cost and complexity of an environmental cooling system. Sensors and control devices mounted on or in aircraft engines, operating at temperatures of 500 to 600°C for periods of up to 100 h, are needed for increased design engineering feedback and diminished testing and maintenance costs. Integration of the additional weight of the required cooling system for Si devices is already a substantial impediment to increased performance in supersonic aircraft. Electronics to be used in planetary space probes must be capable of extended operation at temperatures above 500°C. Consequently, the environmental cooling system for space-based vehicles already accounts for over one-half of current launch vehicle payloads (1-3). The development of devices

intended for operation in high-temperature environments would not only meet these existing needs but would allow many new applications of distributed feedback control.

Due primarily to its wide bandgap (5.5 eV) and unequaled thermal conductivity (20 W/cm²-K), diamond is being investigated for use in high-temperature devices (4). Diamond devices already demonstrated at elevated temperatures include diodes, radiation sensors, thermistors, and transistors (5-9). It also provides radiation hardness for spaceborne nuclear reactors and medical applications. In order for such devices to operate reliably at temperatures above 400°C, more than the material properties alone must be studied. Several important device properties, including the ohmic contact properties, have not yet been investigated at these higher temperatures.

A solid-state reaction process for forming low-resistance, strongly adherent ohmic contacts on diamond has been developed (10-12) and successfully employed on natural bulk diamond samples (13) as well as synthetic diamond

films (14) This process utilizes conventional microelectronic techniques. Briefly, the process begins with the deposition of a thin layer of carbide-forming metal on diamond followed by the deposition of a gold cap layer to protect the metal from corrosion. The carbide-forming metals that have been utilized in forming these contacts include molybdenum, titanium, vanadium, and tantalum. After deposition the contacts are annealed at high temperature in a purified hydrogen ambient. Extensive characterization of the resulting contacts revealed the formation of carbide precipitates at the metal-diamond interface during the anneal. The strong adherence and the low specific contact resistance ($10^{-5} \Omega\text{-cm}^2$) of contacts formed by this process are attributed directly to the carbide precipitates (9, 14, 15). These contacts have been successfully operated at elevated temperatures; here we investigate the long-term reliability of such ohmic contacts in the high-temperature interval, 450 to 625°C.

Experimental Procedure

The sample used in this study was a <100> bulk, p-type semiconducting, (type-IIb) diamond in the shape of a square plate, $5 \times 5 \times 0.25 \text{ mm}^3$. The natural boron concentration is considered to be on the order of $10^{15}/\text{cm}^3$ and the room-temperature carrier concentration on the order of $10^{13}/\text{cm}^3$ (16).

The polished sample was cleaned in a saturated solution of CrO_3 in H_2SO_4 for 10 min at 160°C, followed by a deionized water rinse. This removes any graphitic layers that may be present (13). An acetone rinse and then a soak in boiling methanol for 4 min are then used to remove any surface contaminants. Using plasma-assisted chemical vapor deposition (CVD), a 200 nm layer of silicon nitride was grown on the sample surface. Standard photolithographic techniques and a Shockley transmission line model (TLM) mask were used to pattern openings in the silicon nitride. A 10 nm layer of Mo followed by a 150 nm layer of Au was deposited on the sample in an ion-pumped, UHV evaporating chamber. Electron-beam heating was employed for the Mo layer and resistive heating was used for the Au layer. The pressure during evaporation was 10^{-4} Torr, and the rates of deposition for Au and Mo as measured with a crystal monitor were 0.4 and 0.05 nm/s, respectively. The remaining photoresist and that part of the Mo/Au layer above it were subsequently removed with acetone. A TLM pattern of rectangular $120 \times 300 \mu\text{m}^2$ Mo/Au mesas separated by Si_3N_4 remained on the diamond surface. The sample was then annealed in a purified hydrogen ambient at 950°C for 6 min in order to form the carbide contact. The Si_3N_4 was left in place to prevent possible surface contamination of the diamond during the anneal. The details of the entire process and a discussion of optimum annealing time can be found elsewhere (10, 11).

The sample was mounted in an alumina chip carrier cleaned with organic solvents and held in place with a tungsten clip. Gold wires were wire bonded to Mo/Au contacts separated by distances of 10, 20, and 30 μm . The other ends of the leads were attached to gold-plated pad contacts on the chip carrier. The carrier was then mounted in the apparatus shown in Fig. 1.

This apparatus was designed for variable-temperature, electrical-transport measurements of diamond samples. Strict control of the ambient in the measurement space is essential, not only to prevent oxidation of the metal in the apparatus, but also to prevent the transformation of diamond to graphite which occurs in the presence of oxygen or water vapor at elevated temperatures. There is also mounting evidence that adsorbed gases have a significant effect on the measured electrical properties of diamond (13, 17-21). It is for these reasons that the ambient inside the chamber was limited to purified argon gas. Purified argon is obtained by passing technical-grade argon through a purifier system that employs hot titanium chips. This getter system removes noninert contaminants before the argon enters the measuring space. The purity was monitored continuously by a hygrometer situated in the outgoing gas line. Backflow into the system is prevented by a check valve in the outgo-

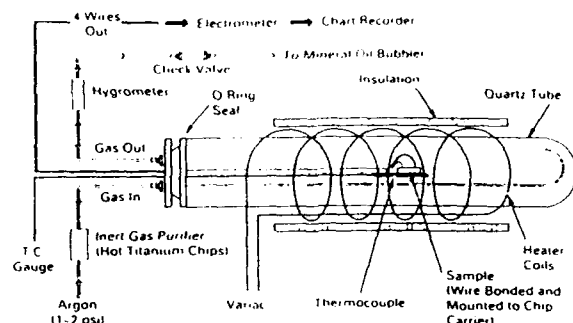


Fig. 1. Apparatus used for electrical resistance measurements of the diamond sample.

ing gas line and a continual positive pressure as monitored by a mineral oil bubbler at the end of the line. These precautionary steps allowed the entire investigation to be performed with the sample ambient at a dew point of less than -115°C (less than 0.3 ppb water weight in air).

The sample was radiatively heated by furnace coils surrounding the quartz chamber. The temperature was controlled by a Variac attached to the furnace coils, and the temperature inside the chamber was measured with a K-type thermocouple in a stainless steel sheath attached to the stainless steel support as shown in Fig. 1. The long annealing times inherent in the experiment provide for adequate thermal equilibrium within the measurement apparatus. Without a feedback mechanism for the furnace coils, the temperature tended to slowly and randomly drift as much as 3% about a mean temperature during the extended measuring periods. Copper electrical leads were fed into the measuring space through an insulating ceramic rod which was sealed at the cold end. These leads were attached to the chip carrier leads using BeCu spring clips. The resistance between contacts was measured with a Keithley 617 electrometer and continuously monitored with a chart recorder. The measuring chamber was shielded from room light to minimize photoconductive effects.

Results and Discussion

The resistance of the sample was continuously monitored for a period of nearly 36 days. The first data were recorded immediately after the sample was placed in the measurement apparatus and before the quartz chamber was purged. The chamber was then purged with the purified argon gas at room temperature for a period of 15 h. This resulted in a vast increase in room-temperature resistance, from 17.2 k Ω before the purge to 790 k Ω afterwards.

The effects of exposure to hydrogen plasma on the electrical characteristics of natural-type IIa (19) and type Ia and type IIb (20) diamond crystals and on synthetic diamond films (18-21) have been the subject of many recent investigations. In those studies, it was demonstrated that this exposure decreases the measured resistance of the diamond sample by as much as five to ten orders of magnitude. It has been suggested that this effect is due to hydrogen passivation of deep level traps, and that high-temperature annealing effectively removes the hydrogen, causing activation of the traps and an accompanying rise in resistivity (19, 20). Using nuclear resonance reaction analysis to determine hydrogen depth profiles in diamond CVD films, Celii *et al.* (21) have concluded that in diamond films, the majority of the hydrogen is not eliminated but is simply displaced to grain boundaries.

Hydrogenation occurs in chemically vapor deposited (CVD) diamond films due to the hydrogen plasma utilized in the growth process (18), but bulk diamond crystals are not routinely exposed to plasmas. The types of plasma used to hydrogenate the diamond samples in the above studies include RF, microwave, and dc plasmas at various temperatures and pressures and for various exposure times. The

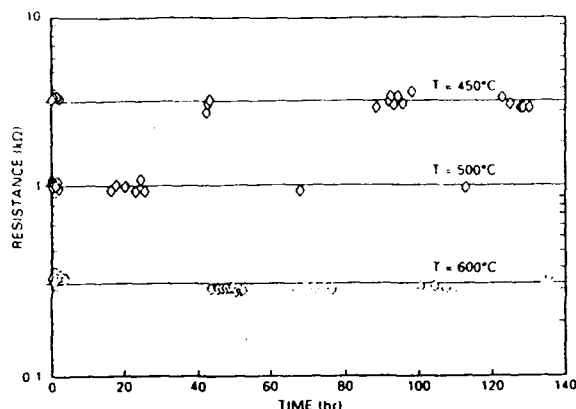


Fig. 2. Resistance vs. time for three temperatures. The solid lines represent the mean temperature during each 140 h measurement. The actual temperature drifted above and below this value $\pm 3\%$.

IIb sample in this study was positioned in an RF plasma created from SiH_4 (silane) and NH_3 for 25 min at 325°C for growth of the silicon nitride layer. The effects of the 950°C anneal in flowing atmospheric pressure H_2 , with respect to hydrogenation, are unknown. It has been suggested that hydrogenation is independent of plasma power and the hydrogen pressure, and it is limited only by the diffusion rate of hydrogen into diamond (20). Where studied, dehydrogenation, or reactivation of the traps has been accomplished with a high-temperature anneal, resulting in the restoration of the high measured resistivity.

The sample used in this investigation was heated over the course of 15 days to 500°C where the resistance eventually stabilized. This stabilization is consistent with the concept of dehydrogenation discussed above. The electrical resistance as a function of annealing time was then measured at three temperatures, 500, 600, and 450°C in that order. Annealing times were in excess of 130 h at each temperature. The resistances between all lead pairs were measured; all pairs exhibited qualitatively identical behavior. The electrical resistance as a function of time at each of these three temperatures is shown in Fig. 2 for contacts with a $50\text{ }\mu\text{m}$ separation. Each solid line represents the mean resistance at a given temperature. The variation of the resistance about each mean temperature is due to the slow variation in furnace temperature noted in the previous section. The resistance simply tracked with that temperature variation. It should also be noted that the maximum temperature investigated was a constraint imposed by the measurement apparatus and not by the sample or the ohmic contacts.

The effect of changes in the electronic properties of the diamond can be seen in Fig. 3 where both the resistance and fluctuations in temperature are plotted as functions of time for the 600°C anneal. The resistance clearly exhibits an inverse relationship with respect to temperature change, as would be expected for semiconducting diamond. Focusing on one fixed temperature over the entire anneal reveals differences in resistances of no more than 1%. It is clear from the resistance data that the contacts are stable against drift or degradation for the times and temperatures investigated.

Conclusion

A previously developed metallization technique was used to form ohmic contacts to a type IIb bulk diamond sample. The resistance between the contacts was measured during thermal annealing times in excess of 130 h at temperatures of 450, 500, and 600°C . The Mo/Au contacts appeared to be stable and reliable at these high temperatures with no indication of deterioration or degradation of performance. Possible indications of hydrogen passivation were observed and a long thermal anneal was used before reported measurements were taken.

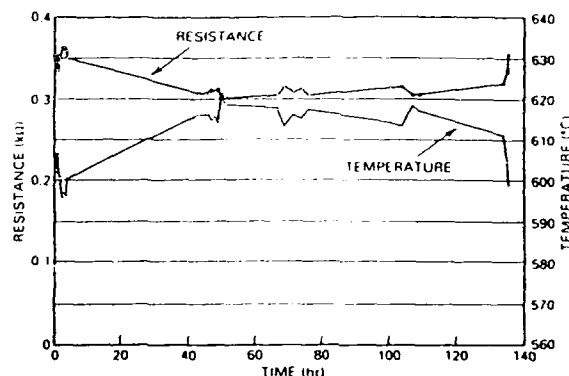


Fig. 3. Resistance and temperature as a function of time near 600°C .

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Ti/TiN Reactive Sputtering: Plasma Emission, X-Ray Diffraction and Modeling

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ABSTRACT

In situ optical emission spectroscopy studies of Ti/TiN reactive sputtering were carried out in a Varian M2000 cluster tool. Deposition rates of Ti/TiN films at temperatures of 25 and 500°C and a pressure of 4.3 mTorr are directly proportional to ratio of Ti(365)/Ar(435) emission lines. Measurement of the ratio of the N(655)/Ar(435) emission lines indicates an incubative dependence on nitrogen flow due to nitridation of the target. X-ray diffraction studies shows an abrupt transition in structure from Ti to TiN as a function of nitrogen flow. TiN reactive sputtering can be accurately described by a mathematical model based on the nitrogen flux balance on target and wall/shield at steady state.

Ti and TiN are used widely as low-contact resistance thin films in integrated circuit applications (1, 2). One of the common techniques to deposit Ti/TiN films is by reactive sputtering in an ambient containing N₂. However, there are still many unknowns about the kinetics and mechanisms of the sputtering process, especially related to the nitridation of the Ti target. In order to repeatably fabricate integrated devices, it is necessary to know the effects of these processes on sputtered film properties and uniformity. In this work, optical emission spectroscopy (OES) is used to monitor active species in the plasma during reactive sputtering. X-ray diffraction (XRD) was used to characterize structural composition of the sputtered films. A mathematical model based on actual geometry and experimental conditions was developed to describe the kinetics of the reactive sputtering process, leading to a better understanding of the process mechanisms.

Experimental

Ti/TiN films were reactively sputtered onto 150 mm diam, p-type, <100> oriented Si wafers in a Varian M2000 sputtering tool using a planar magnetron source (3). The 99.99% Ti target was run at 1 and 3 kW of sputtering power and the deposition times were 450 and 120 s, respectively. The wafers were clamped to a heated stainless steel table with argon injected between the wafer and the table to enhance heat transfer. Ti/TiN films were deposited at a table temperature of 25°C or heated to 500°C with backside argon. The mass flow ratio of the N₂/Ar gas mixture was adjusted from 0-40% with the total pressure maintained at 4.3 mTorr. The total flow rate used was approximately 50 sccm.

Optical emission spectroscopy was carried out with a EG&G model 1235 triple grating spectrograph with a model 1465 intensified multichannel analyzer. Plasma emission was collected via a 1" sapphire window with a mechanical shutter to minimize film deposition on the window. XRD was measured in a Scintag XDS-2000 X-ray diffractometer operating in the Bragg-Brentano configuration using CuK α radiation at 0.15406 nm. Sheet resistance was measured by a four-point probe and thickness was measured with a stylus profilometer.

Experimental Results

The deposition rate of Ti/TiN film at 25 and 500°C was measured as a function of percent of nitrogen flow at 1 and

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3 kW sputtering power (Fig. 1). An abrupt transition from the Ti phase to the TiN phase was observed near 7 and 17% N₂ flow for 1 and 3 kW sputtering power, respectively. Under the same conditions, the OES ratio of the titanium flux Ti (365.4 nm) in the gas phase to the argon flux Ar (434.8 nm), is proportional to the deposition rate, as shown in Fig. 2. This suggests that the sputtered metal flux is a critical control parameter of the reactive sputtering process (4). The difference of unit cell volume per atom for Ti-17.65 Å³ and TiN-19.06 Å³ is within the experimental error of the deposition rate measurement (Fig. 1 and Fig. 2). The ratio of the nitrogen flux N(654.5 nm) to that of argon shows an interesting incubation dependence on nitrogen flow (Fig. 3). The nitrogen emission was found to be barely detectable for N₂ flow below 7 and 17% for 1 and 3 kW sputtering power, respectively. This is consistent with our result of *in situ* measurements of nitrogen partial pressures, using a differentially-pumped mass spectrometer, during TiN reactive sputtering in this system.

The structural features of the Ti/TiN films also exhibited an abrupt phase transition from XRD measurements. At a sputtering power of 1 kW and a deposition temperature of

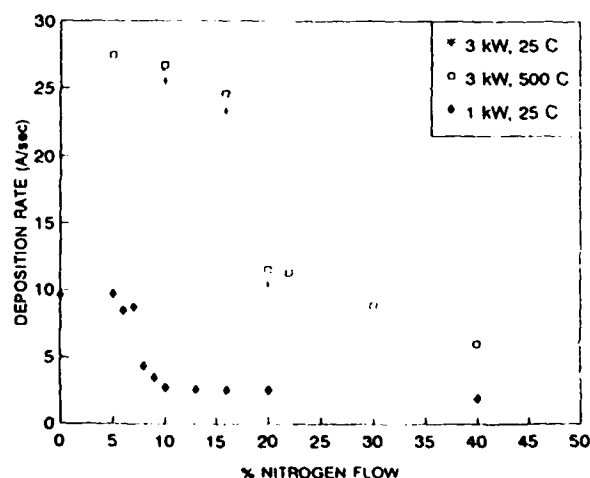


Fig. 1. Deposition rate of Ti/TiN film as a function of nitrogen flow at 1 and 3 kW of sputtering power.